ALKYLIDENE COMPLEXES F RUTHENIUM CONTAINING N-HETEROCYCLIC CARBENE LIGANDS; USE AS HIGHLY ACTIVE, SELECTIVE CATALYSTS FOR OLEFIN METATHESIS

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Description

Alkylidene complexes of ruthenium containing N-heterocyclic carbene ligands; use as highly active, selective catalysts for olefin metathesis

The invention relates to alkylidene complexes of ruthenium containing N-heterocyclic carbene ligands and a process for preparing olefins by olefin metathesis from acyclic olefins having two or more carbon atoms or/and from cyclic olefins having four or more carbon atoms using at least one of these alkylidene complexes as catalyst.

C-C coupling reactions catalyzed by transition metals are among the most important reactions of organic synthetic chemistry. In this context, olefin metathesis makes a significant contribution, since this reaction enables by-product-free olefins to be synthesized. Olefin metathesis has not only a high potential in the area of preparative, organic synthesis (RCM, ethenolysis, metathesis of acyclic olefins) but also in polymer chemistry (ROMP, ADMET, alkyne polymerization). Since its discovery in the 1950s, a number of industrial processes have been able to be realized. Nevertheless, olefin metathesis has developed into a broadly applicable synthetic method only recently due to the discovery of new catalysts (J.C. Mol in: B. Cornils, W.A. Herrmann: Applied Homogeneous Catalysis with Organometallic Compounds, VCH, Weinheim, 1996, p.318-332; M. Schuster, S. Blechert, Angew. Chem. 1997, 109, 2124-2144; Angew. Chem. Int. Ed. Engl. 1997, 36, 2036-2056).

Numerous, fundamental studies have made important contributions to the understanding of this transition metal-catalyzed reaction in which an exchange of alkylidene units between olefins occurs. The generally accepted mechanism involves metal-alkylidene complexes

as active species. These react with olefins to form metallacyclobutane intermediates which undergo cycloreversion to once again form olefins and alkylidene complexes. The isolation of metathesis-active alkylidene and metallacyclobutane complexes supports these mechanistic hypotheses.

Numerous examples may be found, in particular, in the coordination chemistry of molybdenum and tungsten. Specifically the work of Schrock gave well-defined alkylidene complexes whose reactivity can be controlled (J.S. Murdzek, R.R. Schrock, Organometallics 1987, 6, 1373-1374). The introduction of a chiral ligand sphere in these complexes made possible the synthesis of polymers having a high tacticity (K.M. Totland, T.J. Boyd, G.C. Lavoie, W.M. Davis, R.R. Schrock, Macromolecules 1996, 29, 6114-6125). Chiral complexes of the same structural type have also been used successfully in ring-closing metathesis (O. Fujimura, F.J.d.L. Mata, R.H. Grubbs, Organometallics 1996, 15, 1865-1871). However, the high sensitivity toward functional groups, air and water is a drawback.

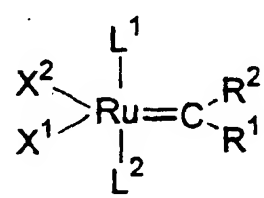
Recently, phosphine-containing complexes of ruthenium have become established (R.H. Grubbs, S.T. Nguyen, L.K. Johnson, M.A. Hillmyer, G.C. Fu, WO 96/04289, 1994; P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs, Angew. Chem., 1995, 107, 2179-2181; Angew. Chem. Int. Ed. Engl. 1995, 34, 2039-2041). Owing to the electron-rich, "soft" character of later transition metals, these complexes have a high tolerance toward hard, functional groups. This is demonstrated, for example, by their use in natural product chemistry (RCM of dienes) (Z. Yang, Y. He, D. Vourloumis, H. Vallberg, K.C. Nicolaou, Angew. Chem. 1997, 109, 170-172; Angew. Chem., Int. Ed. Engl. 1997, 36, 166-168; D. Meng, P. Bertinato, A. Balog, D.S. Su, T. Kamenecka, E.J. Sorensen, S.J. Danishefsky, J. Am. Chem. Soc. 1997, 119, 2733-2734; D. Schinzer, A. Limberg, A. Bauer, O.M. Böhm, M. Cordes,

Angew. Chem. 1997, 109, 543-544; Angew. Chem., Int. Ed. Engl. 1997, 36, 523-524; A. Fürstner, K. Langemann, J. Am. Chem. Soc. 1997, 119, 9130-9136).

However, the range of variation of the phosphine ligands used is very restricted due to steric and electronic factors. Only strongly basic, bulky alkylphosphines such as tricyclohexylphosphine, triisopropylphosphine and tricyclopentylphosphine are suitable for the metathesis of acyclic olefins and relatively unstrained ring systems. Accordingly, the reactivity of these catalysts cannot be adjusted. Chiral complexes of this structural type have also not been able to be obtained.

For these reasons, it is an object of the invention to develop tailored metathesis catalysts which have a high tolerance toward functional groups as a result of a variable ligand sphere and which allow fine adjustment of the catalyst for specific properties of different olefins.

This object is achieved according to the invention by a complex of ruthenium of the structural formula I,



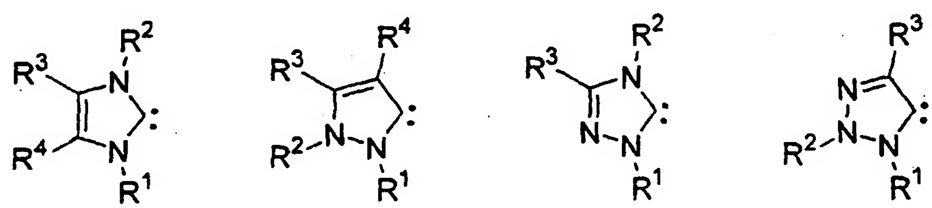
I

where X^1 and X^2 are identical or different and are each an anionic ligand,
R^1 and R^2 are identical or different and can also contain a ring, and R^1 and R^2 are each hydrogen or/and a hydrocarbon group, where the hydrocarbon groups are identical or different and are selected independently from among straight-chain, branched, cyclic or/and

noncyclic radicals from the group consisting of alkyl radicals having from 1 to 50 carbon atoms, alkenyl radicals having from 1 to 50 carbon atoms, alkynyl radicals having from 1 to 50 carbon atoms, aryl radicals having from 1 to 30 carbon atoms and silyl radicals,

where one or more of the hydrogen atoms in the hydrocarbon or/and silyl groups can be replaced independently by identical or different alkyl, aryl, alkenyl, alkynyl, metallocenyl, halogen, nitro, nitroso, hydroxy, alkoxy, aryloxy, amino, amido, carboxyl, carbonyl, thio or/and sulfonyl groups,

the ligand L^1 is an N-heterocyclic carbene of the formulae II-V and the ligand L^2 is an uncharged electron donor, in particular an N-heterocyclic carbene of the formulae II-V or an amine, imine, phosphine, phosphite, stibine, arsine, carbonyl compound, carboxyl compound, nitrile, alcohol, ether, thiol or thioether,



II III IV V

where R^1, R^2, R^3 and R^4 in the formulae II, III, IV and V are identical or different and are each hydrogen or/and a hydrocarbon group,

where the hydrocarbon groups comprise identical or different, cyclic, noncyclic, straight-chain or/and branched radicals selected from the group consisting of alkyl radicals having from 1 to 50 carbon atoms, alkenyl radicals having from 1 to 50 carbon atoms, alkynyl radicals having from 1 to 50 carbon atoms and aryl radicals having from 1 to 30 carbon atoms, in which at least one hydrogen may be replaced by functional groups, and where one or both of R^3 and R^4

may be identical or different halogen, nitro, nitroso, alkoxy, aryloxy, amido, carboxyl, carbonyl, thio or/and sulfonyl groups.

The alkyl radicals, alkenyl radicals or alkynyl radicals in the formulae I to V preferably have from 1 to 20 carbon atoms, particularly preferably from 1 to 12 carbon atoms.

The complexes of the invention are highly active catalysts for olefin metathesis. They are particularly inexpensive. In olefin metathesis, the catalysts of the invention display not only a high tolerance toward a variety of functional groups but also a wide range of possible variations in the ligand sphere. Variation of the preparatively readily obtainable N-heterocyclic carbene ligands enables activity and selectivity to be controlled in a targeted manner and, in addition, chirality can be introduced in a simple way.

The anionic ligands X^1 and X^2 of the complex of the invention, which are identical or different, are preferably each halide, pseudohalide, tetraphenylborate, perhalogenated tetraphenylborate, tetrahaloborate, hexahalophosphate, hexahaloantimonate, trihalomethanesulfonate, alkoxide, carboxylate, tetrahaloaluminate, tetracarbonylcobaltate, hexahaloferrate(III), tetrahaloferrate(III) or/and tetrahalopalladate(II),
with preference being given to halide, pseudohalide, tetraphenylborate, perfluorinated tetraphenylborate, tetrafluoroborate, hexafluorophosphate, hexafluoroantimonate, trifluoromethanesulfonate, alkoxide, carboxylate, tetrachloroaluminate, tetracarbonylcobaltate, hexafluoroferrate (III), tetrachloroferrate(III) or/and tetrachloropalladate(II) and preferred pseudohalides being cyanide, thiocyanate, cyanate, isocyanate and isothiocyanate.

In the formulae II, III, IV and V, some or all of the hydrogen in the hydrocarbon groups R^1, R^2, R^3 and R^4 can be replaced independently by identical or different halogen, nitro, nitroso, hydroxy, alkoxy, aryloxy, amino, amido, carboxyl, carbonyl, thio, sulfonyl or/and metallocenyl groups. In these formulae, R^3 and R^4 can form a fused-on ring system.

The ligands L^1 and L^2 of the complex of the structural formula I can form a chelating ligand of the formula VI

$$L^1—Y—L^2$$
VI

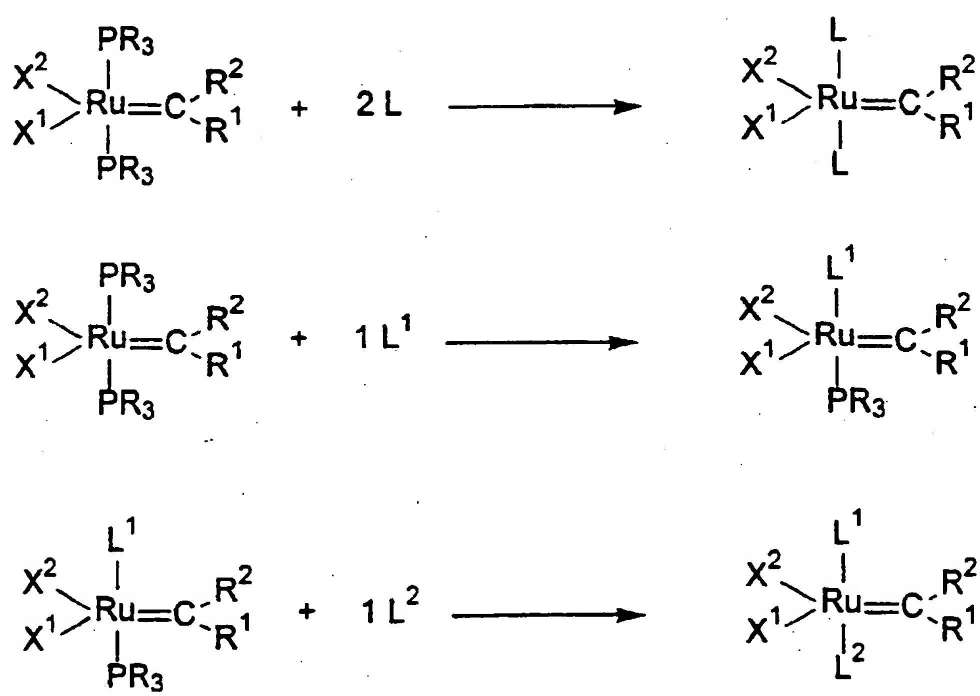
where the bridges Y can comprise cyclic, noncyclic, straight-chain or/and branched radicals selected from the group consisting of alkylene radicals having from 1 to 50 carbon atoms, alkenylene radicals having from 1 to 50 carbon atoms, alkynylene radicals having from 1 to 50 carbon atoms, arylene radicals having from 1 to 30 carbon atoms, metallocenylene, borylene and silylene radicals in which one or more hydrogens may be replaced independently by identical or different alkyl, aryl, alkenyl, alkynyl, metallocenyl, halo, nitro, nitroso, hydroxy, alkoxy, aryloxy, amino, amido, carboxyl, carbonyl, thio or/and sulfonyl groups, preferably alkyl, aryl or/and metallocenyl groups.

The ligands of the formulae II, III, IV, V or/and VI can have central, axial or/and planar chirality.

In the structural formula I of the complex, R^1 and R^2 are preferably hydrogen, substituted or/and unsubstituted alkyl, alkenyl or/and aryl radicals, X^1 and X^2 are preferably halide, alkoxide or/and carboxylate ions and L^1 and L^2 are preferably each an N-heterocyclic carbene of the formula II.

The complexes are usually synthesized by ligand replacement in corresponding phosphine complexes. Two phosphine ligands can be replaced selectively in accordance with the reaction equation (1) or only one can be replaced in accordance with reaction equation (2). In the case of single replacement, the second phosphine can be replaced selectively by another electron donor, e.g. pyridine, phosphine, N-heterocyclic carbene, phosphite, stibene, arsine, in accordance with reaction equation (3).

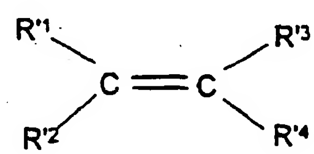
In particular, this route makes it possible for the first time to prepare chiral, metathesis-active catalysts based on ruthenium (example complexes 2 and 3).



The complexes of the invention are found to be extremely efficient catalysts in olefin metathesis. The excellent metathesis activity is demonstrated in the examples by means of a number of examples of different metathesis reactions.

The present invention therefore also encompasses processes for all olefin metathesis reactions such as ring-opening metathesis polymerization (ROMP), metathesis of acyclic olefins, ethenolysis, ring-closing metathesis (RCM), acyclic diene metathesis polymerization (ADMET) and depolymerization of olefin polymers. The high stability and tolerance of the complexes of the invention toward functional groups, in particular alcohol, amine, thiol, ketone, aldehyde, carboxylic acid, ester, amide, ether, silane, sulfide and halogen groups, makes it possible for such functional groups to be present during the metathesis reaction.

The object of the invention is also achieved by a process for preparing acyclic olefins having two or more carbon atoms or/and cyclic olefins having four or more carbon atoms, in each case of the formula VII



VII

VII

from acyclic olefins having two or more carbon atoms or/and from cyclic olefins having four or more carbon atoms, in each case corresponding to the formula VII by an olefin metathesis reaction in the presence of at least one catalyst, wherein
a catalyst as claimed in any one of claims 1 to 7 is used and R'^1, R'^2, R'^3 and R'^4 in the formula VII are hydrogen or/and hydrocarbon groups,
where the hydrocarbon group is each selected independently from among straight-chain, branched, cyclic or/and noncyclic radicals of the group consisting of alkyl radicals having from 1 to 50 carbon atoms, alkenyl radicals having from 1 to 50 carbon

atoms, alkynyl radicals having from 1 to 50 carbon atoms, aryl radicals having from 1 to 30 carbon atoms, metallocenyl or/and silyl radicals, in which one or more hydrogens may be replaced by a functional group, where one or more of R'^1, R'^2, R'^3 and R'^4 may independently be identical or different halogen, nitro, nitroso, hydroxy, alkoxy, aryloxy, amino, amido, carboxyl, carbonyl, thio, sulfonyl or/and metallocenyl groups.

The olefins used preferably contain one or more double bonds. In particular, R'^1, R'^2, R'^3 and R'^4 in the olefins of the formula VII to be prepared form, in pairs, one or more identical or different rings.

Preferably, some or all of the hydrogen atoms in the hydrocarbon groups R'^1, R'^2, R'^3 and R'^4 of the olefins of the formula VII to be prepared are replaced independently by identical or different halogen, silyl, nitro, nitroso, hydroxy, alkoxy, aryloxy, amino, amido, carboxyl, carbonyl, thio, sulfonyl or/and metallocenyl groups.

The process of the invention can be carried out in the presence or absence of solvents, but preferably in the presence of organic solvents. The process of the invention can advantageously be carried out with addition of a Brönsted acid, preferably HCl, HBr, HI, HBF_4, HPF_6 or/and trifluoroacetic acid, or/and with addition of a Lewis acid, preferably BF_3, $AlCl_3$ or/and ZnI_2.

Surprisingly, this makes it possible for the first time to tailor a wide variety of olefins individually to different properties on the basis of small variations in the catalysis conditions or/and the catalysts, since the process of the invention for preparing olefins has an unexpectedly high tolerance toward functional groups.

Examples:

The following examples illustrate the invention but do not restrict its scope.

1) Preparation of the complex of the invention

General procedure:
1 mmol of $(PPh_3)_2Cl_2Ru(=CHPh)$ was dissolved in 20 ml of toluene and admixed with a solution of 2.2 equivalents of the appropriate imidazolin-2-ylidene in 5 ml of toluene. The reaction solution was stirred at room temperature RT for 45 minutes, subsequently evaporated to about 2 ml and the crude product was precipitated using 25 ml of pentane. The crude product was taken up in 2 ml of toluene and precipitated using 25 ml of pentane a number of times. The residue was extracted with toluene, the solution was evaporated to dryness, washed twice with pentane and dried for a number of hours in a high vacuum.

The data from low-temperature NMR spectra are mostly reported for characterization, since the spectra at room temperature sometimes did not give all the information because of dynamic effects.

The following compounds are prepared by the abovedescribed general procedure:

1a) Benzylidenedichlorobis(1,3-diisopropylimidazolin-2-ylidene)ruthenium
- complex 1:
Yield: 487 mg (0.86 mmol = 86% of theory)
Elemental analysis EA for $C_{25}H_{38}Cl_2N_4Ru$ (566.58):

found	C 53.21	H 6.83 N 9.94;
calculated	C 53.00	H 6.76 N 9.89.

^{1}H-NMR (CD_2Cl_2/200 K): δ 20.33 (1H, s, Ru=CH), 8.25 (2H, d, $^3J_{HH}$ = 7.6 Hz, o-H of C_6H_5), 7.63 (1H, t, $^3J_{HH}$ =

7.6 Hz, *p*-H of C_6H_5), 7.34 (2H, t, *m*-H of C_6H_5, $^3J_{HH}$ = 7.6 Hz), 7.15 (2H, br, NCH), 7.03 (2H, br, NCH), 5.97 (2H, spt, $^3J_{HH}$ = 6.4 Hz, NC*H*Me$_2$), 3.73 (2H, spt, $^3J_{HH}$ = 6.4 Hz, NC*H*Me$_2$), 1.64 (12H, d, $^3J_{HH}$ = 6.4 Hz, NCH*Me*$_2$), 1.11 (6H, d, $^3J_{HH}$ = 6.4 Hz, NCH*Me*$_2$), 0.75 (6H, d, $^3J_{HH}$ = 6.4 Hz, NCH*Me*$_2$).

^{13}C-NMR (CD_2Cl_2/200 K): δ 295.6 (Ru=CH), 183.5 (NCN), 151.6 (*ipso*-C of C_6H_5), 129.5, 128.6 and 128.1 (*o*-C, *m*-C and *p*-C of C_6H_5), 118.1 and 117.2 (NCH), 52.1 and 50.1 (N*C*HMe$_2$), 24.5, 23.8, 23.8 and 22.4 (NCH*Me*$_2$).

1b) Benzylidenedichlorobis(1,3-di((R)-1'-phenylethyl)-imidazolin-2-ylidene)ruthenium
- complex <u>2</u>:
Yield: 676 mg (0.83 mmol = 83% of theory)
EA for $C_{45}H_{46}Cl_2N_4Ru$(814.86):

found	C 66.48	H 5.90	N 6.73;
calc.	C 66.33	H 5.69	N 6.88.

^{1}H-NMR (CD_2Cl_2/200 K): δ 20.26 (1H, s, Ru=CH), 8.13 (2H, br, *o*-H C_6H_5), 7.78 - 6.67 (29H, of which 2*m*-H and 1*p*-H of C_6H_5, 20H of NCHMe*Ph*, 2H of NC*H*MePh and 4H of NCH), 4.91 (2H, m, NC*H*MePh), 1.84 (3H, d, $^3J_{HH}$ = 6.6 Hz, NCH*Me*Ph), 1.81 (3H, d, $^3J_{HH}$ = 6.6 Hz, NCH*Me*Ph), 1.51 (3H, d, $^3J_{HH}$ = 6.6 Hz, NCH*Me*Ph), 1.21 (3H, d, $^3J_{HH}$ = 6.6 Hz, NCH*Me*Ph).

^{13}C-NMR (CD_2Cl_2/200 K): δ 294.7 (Ru=CH), 186.0 and 185.6 (NCN), 151.2 (*ipso*-C of C_6H_5), 141.2, 140.3, 140.1 and 139.9 (ipso-C of NCHMe*Ph*), 133.1 - 125.9 (*o*-C, *m*-C, *p*-C of C_6H_5 and NCHMe*Ph*), 120.5, 119.9, 119.2 and 118.8 (NCH), 57.6, 57.4, 56.7 and 56.1 (NCHMePh), 22.2, 20.6, 20.4 and 20.3 (NCH*Me*Ph).

1c) Benzylidenedichlorobis(1,3-di-((R)-1'-naphthyl-ethyl)imidazolin-2-ylidene)ruthenium
- complex <u>3</u>:
Yield: 792 mg (0.78 mmol = 78% of theory)
EA for $C_{61}H_{54}Cl_2N_4Ru$(1015.1):

found	C 72.34	H 5.46	N 5.45;
calc.	C 72.18	H 5.36	N 5.52.

^{1}H-NMR (CD_2Cl_2/260 K): δ 20.90 (1H, s, Ru=CH), 8.99 (2H, br, *o*-H of C_6H_5), 8.2 - 5.6 (39H, of which 2*m*-H and 1*p*-H of C_6H_5, 28H of NCHMe*Naph*, 4H of NCH and 4H of NC*H*MeNaph), 2.5 - 0.8 (12H, m, NCH*Me*Naph).
^{13}C-NMR (CD_2Cl_2/260 K): δ 299.9 (Ru=CH), 187.2 and 184.7 (NCN), 152.0 (*ipso*-C of C_6H_5), 136.0 - 124.0 (*o*-C, *m*-C, *p*-C of C_6H_5 and NCHMe*Naph*), 121.7, 121.0, 119.9, and 118.9 (NCH), 56.7, 56.1, 55.0 and 54.7 (N*C*HMeNaph), 24.7, 24.3, 21.0 and 20.0 (NCH*Me*Naph).

For the following complexes, slight deviations from the general procedure are necessary:

1d) (4-Chlorobenzylidene)dichlorobis(1,3-diisopropylimidazolin-2-ylidene)ruthenium
- complex 4:
1 mmol of $(PPh_3)_2Cl_2Ru[=CH(p\text{-}C_6H_4Cl)]$ was used as starting material. The further procedure corresponded to the abovedescribed general procedure.
Yield: 535 mg (0.89 mmol = 89% of theory)
EA for $C_{24}H_{38}Cl_3N_4Ru$ (601.03):
found C 48.13 H 6.33 N 9.24;
calc. C 47.96 H 6.37 N 9.32.
^{1}H-NMR (CD_2Cl_2/ 200 K): δ 20.33 (1H, s, Ru=CH), 8.25 (2H, d, $^3J_{HH}$ = 7.6 Hz, *o*-H of C_6H_4Cl), 7.63 (1H, t, $^3J_{HH}$ = 7.6 Hz, *m*-H of C_6H_4Cl), 7.15 (2H, br, NCH), 7.03 (2H, br, NCH), 5.97 (2H, spt, $^3J_{HH}$ = 6.4 Hz, NC*H*Me_2), 3.73 (2H, spt, $^3J_{HH}$ = 6.4 Hz, NC*H*Me_2), 1.64 (12H, d, $^3J_{HH}$ = 6.4 Hz, NCH*Me*$_2$), 1.11 (6H, d, $^3J_{HH}$ = 6.4 Hz, NC*H*Me_2), 0.75 (6H, d, $^3J_{HH}$ = 6.4 Hz, NCH*Me*$_2$).
^{13}C-NMR (CD_2Cl_2/ 200 K): δ 295.6 (Ru=CH), 183.5 (NCN), 151.6 (*ipso*-C of C_6H_4Cl), 134.3 (*p*-C of C_6H_4Cl), 128.6 and 128.1 (*o*-C and *m*-C of C_6H_4Cl), 118.1 and 117.2 (NCH), 52.1 and 50.1 (N*C*HMe_2), 24.5, 23.8, 23.8 and 22.4 (NCH*Me*$_2$).

1e) Benzylidenedichlorobis(1,3-dicyclohexylimidazolin-2-ylidene)ruthenium
- complex 5:

1 mmol of $(PPh_3)_2Cl_2Ru(=CHPh)$ was dissolved in 25 ml of toluene and admixed with a solution of 2.2 equivalents of 1,3-dicyclohexylimidazolin-2-ylidene in 5 ml of toluene. The reaction solution was stirred at RT for 45 minutes and subsequently freed of the solvent. Unlike the general procedure, the crude product was purified by flash chromatography.

Yield: 305 mg (0.42 mmol = 42% of theory)

EA for $C_{37}H_{54}Cl_2N_4Ru$ (726.84):

found C 61.23 H 7.56 N 7.87;

calc. C 61.14 H 7.49 N 7.71.

^{1}H-NMR (CD_2Cl_2/ 298 K): δ 20.45 (1H, s, Ru=CH), 8.31 (2H, d, $^3J_{HH}$ = 7.6 Hz, *o*-H- of C_6H_5), 7.63 (1H, t, $^3J_{HH}$ = 7.6 Hz, *p*-H- of C_6H_5), 7.34 (2H, t, $^3J_{HH}$ = 7.6 Hz, *m*-H- of C_6H_5), 7.14 (2H, br, NCH), 7.00 (2H, br, NCH), 6.06 (2H, br, CH of NC_6H_{11}), 3.82 (2H, br, CH of NC_6H_{11}), 1.64 (12H,br,CH_2 of NC_6H_{11}), 0.93 (12H, br, CH_2 of NC_6H_{11}).

^{13}C-NMR (CD_2Cl_2/ 298 K): δ 299.4 (Ru=CH), 182.9 (NCN), 152.0 (*ipso*-C of C_6H_5), 131.1, 129.8 and 129.1 (*o*-C, *m*-C and *p*-C of C_6H_5), 118.3 and 117.8 (br, NCH), 59.6 and 57.5 (br, CH of NC_6H_{11}), 35.7, 26.9 and 25.6 (br, CH_2 of NC_6H_{11}).

1f) Benzylidenedichloro(1,3-di-tert-butylimidazolin-2-ylidene)(triphenylphosphine)ruthenium

- complex <u>6</u>:

1 mmol of $(PPh_3)_2Cl_2Ru(=CHPh)$ was dissolved in 20 ml of toluene and admixed with a solution of 1.1 equivalents of 1,3-di-tert-butylimidazolin-2-ylidene in 5 ml of toluene. The reaction solution was stirred at RT for 30 minutes, subsequently evaporated to about 2 ml and the crude product was precipitated using 25 ml of pentane. The further work-up was carried out as described in the general procedure.

Yield: 493 mg (0.70 mmol = 70% of theory)

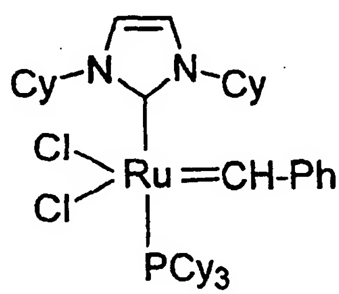
EA for $C_{36}H_{41}Cl_2N_2P_1Ru$ (704.69):

found C 61.12 H 5.55 N 3.62 P 4.59

calc. C 61.36 H 5.86 N 3.98 P 4.38.

^{1}H-NMR (CD_2Cl_2/ 200 K): δ 20.70 (1H, s, Ru=CH), 8.03 (2H, d, $^3J_{HH}$ = 7.6 Hz, *o*-H of C_6H_5), 7.50 - 6.95 (20 H, of which 2*m*-H and 1*p*-H of C_6H_5, 15H of PPh_3 and 2H of NCH), 1.86 (9H, s, $NCMe_3$), 1.45 (9H, s, $NCMe_3$).
^{13}C-NMR (CD_2Cl_2/ 200 K): δ 307.4 (br, Ru=CH), 178.3 (d, J_{PC} = 86 Hz, NCN), 151.5 (d, J_{PC} = 4.5 Hz, *ipso*-C of C_6H_5), 135.0 (m, *o*-C of PPh_3), 131.9 (m, *ipso*-C of PPh_3), 130.2 (s, *p*-C of PPh_3), 129.5, 128.6 and 128.1 (s, *o*-C, *m*-C and *p*-C of C_6H_5), 128.0 (m, *m*-C of PPh_3), 117.7 and 117.6 (NCH), 58.7 and 58.5 ($NCMe_3$), 30.0 and 29.5 ($NCMe_3$).
^{31}P-NMR (CD_2Cl_2/ 200 K): δ 40.7 (s, PPh_3).

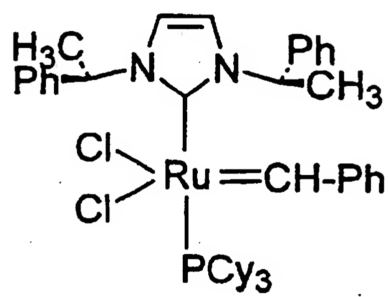
1g) Benzylidenedichloro-(1,3-dicyclohexylimidazolin-2-ylidene)(tricyclohexylphosphine)ruthenium



A solution of 1.2 mmol of dicyclohexylimidazolin-2-ylidene is added dropwise at -78°C to 1 mmol of $RuCl_2(PCy_3)_2(CHPh)$ in 100 ml of THF. The mixture is slowly warmed to room temperature over a period of 5 hours and the solvent is subsequently removed. The crude product is extracted with a mixture of 2 ml of toluene and 25 ml of pentane and the product is precipitated from this solution at -78°C.
Yield: 0.80 mmol (80% of theory)
EA for $C_{40}H_{63}Cl_2N_2PRu$:
found C 61.99, H 8.20, N 3.62; calc. C 61.11; H 8.29; N 3.59.
^{1}H NMR (CD_2Cl_2 / 25°C): δ = 20.30 (1H, d, $^3J_{PH}$ = 7.4 Hz, Ru=CH), 8.33 (2H, d, $^3J_{HH}$ = 7.4 Hz, *o*-H of C_6H_5), 7.62 (1H, t, $^3J_{HH}$ = 7.4 Hz, *p*-H of C_6H_5), 7.33 (2H, t, $^3J_{HH}$ =

7.4 H_2, *o*-H of C_6H_5), 7.11 (1H, s, NCH), 6.92 (1H, s, NCH), 5.97 (1H, m, CH of NC_6H_{11}), 3.36 (1H, m, CH of NC_6H_{11}), 2.42 (3H, m, CH of PCy_3), 1.90-0.89 (50H, all m, CH_2 of NC_6H_{11} and PCy_3).
^{13}C NMR (CD_2Cl_2 / 25°C): d = 298.7 (Ru=CH), 181.2 (d, J_{PC} = 88 Hz, NCN), 152.5 (*ipso*-C of C_6H_5), 130.8, 129.8, and 129.2 (*o*-C, *m*-C, and *p*-C of C_6H_5), 118.9 and 118.0 (NCH), 59.5 and 57.7 (CH of NC_6H_{11}) 33.2 (d, J_{PC} = 17 Hz, *ipso*-C of PCy_3), 29.9 (s, *m*-C of PCy_3), 26.8 (d, J_{PC} = 3.7 Hz, *o*-C of PCy_3), 25.4 (s, *p*-C of PCy_3) 34.9, 33.3, 33.1, 28.2, 28.1, and 25.7 (CH_2 of NC_6H_{11}).
^{31}P NMR (CD_2Cl_2 / 25°C): d = 28.2.

1h) Benzylidenedichloro(1,3-di-((R)-1'-phenylethyl)-imidazolin-2-ylidene)(tricyclohexylphosphine)ruthenium



A solution of 1.2 mmol of di-(*R*)-1'-phenylethylimidazolin-2-ylidene is added dropwise at -78°C to 1 mmol of $RuCl_2(PCy_3)_2(CHPh)$ in 100 ml of THF. The mixture is slowly warmed to room temperature over a period of 5 hours and the solvent is subsequently removed. The crude product is extracted with a mixture of 2 ml of toluene and 25 ml of pentane and the product is precipitated from this solution at -78°C.
Yield: 0.74 mmol (74% of theory)
EA for $C_{44}H_{59}Cl_2N_2PRu$:
calc. C 64.53, H 7.27, N 3.42; found C 64.58, H 7.34, N 3.44.

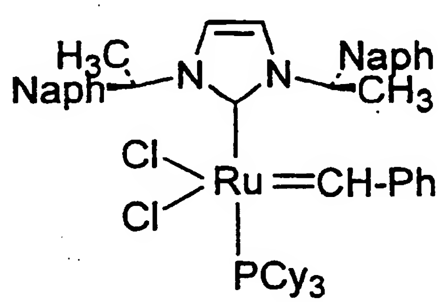
^1H NMR(CD_2Cl_2/ 25°C): d 20.19 (1H, d, $^3J_{PH}$ = 4.5 Hz, Ru=CH), 7.74 - 7.00 (15H, all m, CH of C_6H_5), (1H, m,

NC*H*MePh), 6.73 (1H, s, NCH), 6.70 (1H, s, NCH), 2.52 (1H, m, NC*H*MePh), 2.44 (3H, m, CH of PCy_3), 2.11 (3H, d, $^3J_{HH}$ = 6.8 Hz, NCH*Me*Ph), 1.82-1.12 (30H, all m, CH_2 of PCy_3)1.35 (3H, d, $^3J_{HH}$ = 6.8 Hz, NCH*Me*Ph).

^{13}C NMR (CD_2Cl_2 / 25°C): δ = 292.7 (Ru=CH), 183.4 (d, J_{PC} = 78 Hz, NCN), 151.8 (*ipso*-C of C_6H_5), 140.1 and 139.5 (*ipso*-C of NCHME*Ph)*, 129.5, 128.5, 128.3, 127.9, 127.5, 127.4, 127.2, 126.6, and 126.1 (*o*-C, *m*-C and *p*-C of C_6H_5) 119.8 and 118.4 (NCH), 57.4 and 56.2 (N*C*HMePh), 31.3(d, J_{PC} = 17 Hz, *ipso*-C of PCy_3), 29.0 (s, *m*-C of PCy_3), 28.9 (s, *m*-C of PCy_3), 27.2 (d, J_{PC} = 3.7 Hz, *o*-C of PCy_3), 27.0 (d, J_{PC} = 3.7 Hz, *o*-C of PCy_3), 25.8 (s, *p*-C of PCy_3) 21.7 and 20.3 (NCH*Me*Ph).

^{31}P NMR (CD_2Cl_2 / 25°C): δ 38.1.

1i) Benzylidenedichloro(1,3-di-((R)-1'-naphthylethyl)-imidazolin-2-ylidene)(tricyclohexylphosphine)ruthenium



A solution of 1.2 mmol of di-(R)-1'-naphthylethylimidazolin-2-ylidene is added dropwise at -78°C to 1 mmol of $RuCl_2(PCy_3)_2(CHPh)$ in 100 ml of THF. The mixture is slowly warmed to room temperature over a period of 5 hours and the solvent is subsequently removed. The crude product is extracted with a mixture of 2 ml of toluene and 25 ml of pentane and the product is precipitated from this solution at -78°C.

Yield: 0.72 mmol (72% of theory)

EA for $C_{52}H_{63}Cl_2N_2PRu$:

calc. C 67.95, H 6.91, N 3.05; found C 68.09, H 7.02, N 3.04.

^1H NMR (CD_2Cl_2/ 25°C): δ 20.33 (1H, d, $^3J_{HH}$ = 5.4 Hz, Ru=CH), 8.88 (2H, d, $^3J_{HH}$ = 8.0 Hz, *o*-H of C_6H_5) 7.94 - 6.96 (17H, all m, CH of C_6H_5), 6.70 (1H, s, NCH), 6.61 (1H, s, NCH), 5.83 (1H, m, NC*H*MeNaph), 2.59 (1H, m, NC*H*MeNaph), 2.49 (3H, m, CH of PCy_3), 2.44 (3H, d, $^3J_{HH}$ = 6.8 Hz, NCH*Me*Naph), 1.95-1.01 (30H, all m, CH_2 of PCy_3)1.54 (3H, d, $^3J_{HH}$ = 6.8 Hz, NCH*Me*Naph).

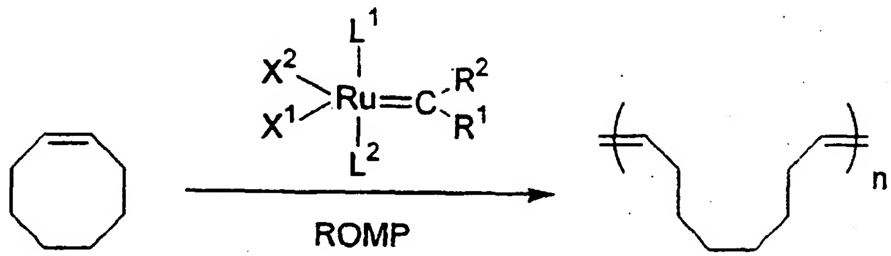
^{13}C NMR (CD_2Cl_2 / 25°C): δ = 298.4 (Ru=CH), 184.0 (d, J_{PC} = 87 Hz, NCN), 152.3 (*ipso*-C of C_6H_5), 138.3 and 137.6 (*ipso*-C of NCHMe*Naph*), 134.3 - 122.9 (*o*-C, *m*-C, and *p*-C of C_6H_5, CHMe*Naph*) 120.6 and 119.5 (NCH), 56.4 and 55.7 (N*C*HMeNaph), 32.5(d, J_{PC} = 17 Hz, *ipso*-C of PCy_3), 30.1 (s, *m*-C of PCy_3), 30.0 (s, *m*-C of PCy_3), 28.1 (pseudo-t, J_{PC} = 7.4 Hz, *o*-C of PCy_3), 26.8 (s, *p*-C of PCy_3) 24.0 and 22.7 (NCH*Me*Naph).

^{31}P NMR (CD_2Cl_2 / 25°C): δ = 31.8.

2) Use of the complex of the invention in olefin metathesis

The following examples demonstrate the potential of the complexes of the invention in olefin metathesis. The advantage of these complexes of the invention compared to phosphine-containing complexes is the targeted and inexpensive variation of the radicals R on the nitrogen atoms of the N-heterocyclic carbene ligands. This tailoring of the catalysts of the invention on the basis of individual properties of the olefins to be subjected to metathesis enables both activity and selectivity of the reaction to be controlled.

2a) Ring-opening metathesis polymerization (ROMP): Norbornene, cyclooctene and functionalized norbornene derivatives serve as examples.



(4)

<u>Typical reaction procedure for the polymerization of cyclooctene (or norbornene):</u>

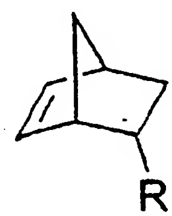
410 µl (3.13 mmol) of cyclooctene were added to a solution of 3.6 mg (6.3 µmol) of <u>1</u> in 0.5 ml of methylene chloride. After about 10 minutes, a highly viscous gel which could no longer be stirred had formed. 1 ml of methylene chloride was added. This procedure was repeated whenever the stirrer was no longer able to operate (a total of 3 ml of methylene chloride). After 1 hour, 5 ml of methylene chloride to which small amounts of tert-butyl ether and 2,6-di-tert-butyl-4-methylphenol had been added were introduced. After a further 10 minutes, the solution was slowly added dropwise to a large excess of methanol, the mixture was filtered and the solid was dried in a high vacuum for a number of hours.
Yield: 291 mg (2.64 mmol = 84.3% of theory)

Table 1. Polymerization of norbornene and cyclooctene

Example	Complex	Monomer	Ratio of [monomer]/[cat.]	Reaction time t	Yield
2.1a	<u>1</u>	Norbornene	100 : 1	1 min	91%
2.1b	<u>5</u>	Norbornene	100 : 1	1 min	92%
2.1c	<u>1</u>	Cyclooctene	500 : 1	1 h	84%
2.1d	<u>1</u>	Cyclooctene	500 : 1	2 h	97%
2.1e	<u>5</u>	Cyclooctene	500 : 1	1 h	87%

<u>Typical reaction procedure for the polymerization of functionalized norbornene derivatives:</u>

The formula VIII shows the basic skeleton of the norbornene derivatives used in Table 2.



VIII

0.3 ml of a solution of 432 mg (3.13 mmol) of 5-carboxyl-2-norbornene (formula VIII with R = CO_2H) in methylene chloride was added to a solution of 3.6 mg (6.3 µmol) of <u>1</u> in 0.2 ml of methylene chloride. After about 10 minutes, a highly viscous gel which could no longer be stirred had formed. A further 0.5 ml of methylene chloride was added. This procedure was repeated whenever the stirrer was no longer able to operate. After 1 hour, 5 ml of methylene chloride to which small amounts of tert-butyl ether and 2,6-di-tert-butyl-4-methylphenol had been added were introduced. After a further 10 minutes, the solution was slowly added dropwise to a large excess of methanol, filtered and the solid was dried in a high vacuum for a number of hours.

Yield: 423 mg (3.06 mmol = 98.1% of theory)

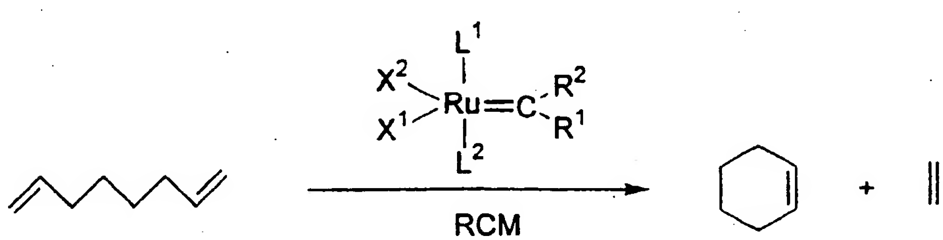
The reactions at 50°C were carried out in an analogous manner in dichloroethane instead of methylene chloride.

Table 2. Polymerization of functionalized norbornene derivatives

Example	Complex	Radical R in formula VIII	T[°C]	Reaction time t	Yield
2.1f	1	O_2CCH_3	25	30 min	99%
2.1g	1	CH_2OH	25	2 h	15%
2.1h	1	CH_2OH	50	2 h	18%
2.1i	1	CHO	25	2 h	36%
2.1k	1	CHO	50	2 h	52%
2.1l	1	$COCH_3$	25	2 h	42%
2.1m	1	$COCH_3$	50	2 h	67%
2.1n	1	CO_2H	25	2 h	98%

The polymerization of norbornene occurred in seconds. In the polymerization of cyclooctene, virtually quantitative conversions were obtained within one hour (Table 1). Differences in activity can be detected by use of various complexes under dilute conditions and demonstrate the dependence of the activity on the substitution pattern of the carbene ligands used. The high stability and tolerance toward functional groups is demonstrated by the polymerization of functionalized norbornene derivatives containing ester, alcohol, aldehyde, ketone or/and carboxylic acid groups (Table 2). Here, monomers of the formula VIII with R = CH_2OH, CHO and CO_2H were able to be polymerized for the first time.

2.2) Ring-closing metathesis (RCM) of 1,7-octadiene:



(5)

<u>Typical reaction procedure for RCM of 1,7-octadiene:</u>

A solution of 3.6 mg (6.3 µmol) of <u>1</u> in 2 ml of dichloroethane was admixed with 46 µl (0.31 mmol) of 1,7-octadiene, and the reaction mixture was placed in an oil bath at 60°C. After one hour, the reaction mixture was analyzed by GC/MS.

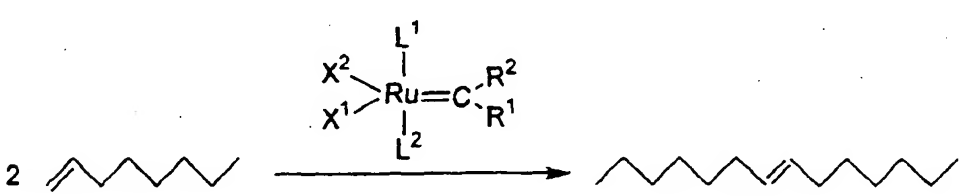
Table 3. RCM of 1,7-octadiene (octadiene/catalyst = 50:1)

Example	Complex	Solvent	T[°C]	Reaction time t	Yield
2.2a	<u>1</u>	Methylene chloride	25	5.5 h	51%
2.2b	<u>1</u>	Methylene chloride	25	24 h	70%
2.2c	<u>1</u>	Dichloroethane	60	1 h	99%
2.2d	<u>2</u>	Dichloroethane	60	1 h	99%
2.2e	<u>3</u>	Dichloroethane	60	1 h	99%
2.2f	<u>5</u>	Dichloroethane	60	1 h	99%

The potential in ring-closing metathesis was illustrated by the reaction of 1,7-octadiene to form cyclohexene with liberation of ethylene (Table 3). <u>1</u> gave a yield of 51% after 5.5 hours; at 60°C, all complexes of the invention used gave quantitative conversions.

2.3) Metathesis of acyclic olefins

A) Metathesis of 1-octene:



1- ctene 7-tetradec ne

(6)

Typical reaction procedure for the metathesis of 1-octene:

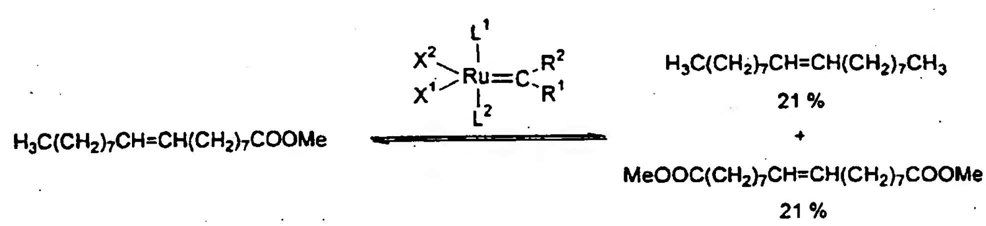
A solution of 3.6 mg (6.3 µmol) of 1 in 2 ml of dichloroethane was admixed with 49 µl (0.31 mmol) of 1-octene, and the reaction mixture was placed in an oil bath at 60°C. After 3 hours, the reaction mixture was analyzed by GC/MS.

Table 4. Homometathesis of 1-octene (octene/catalyst = 50:1)

Example	Complex	T[°C]	Reaction time t	Conversion of 1-octene	Selectivity [a]
2.3a	2	60	1 h	31%	98%
2.3b	2	60	2 h	58%	97%
2.3c	1	60	1 h	83%	73%
2.3d	1	60	3 h	97%	63%

[a] The selectivity indicates the proportion of 7-tetradecene compared to other metathesis products

B) Metathesis of methyl oleate:



(7)

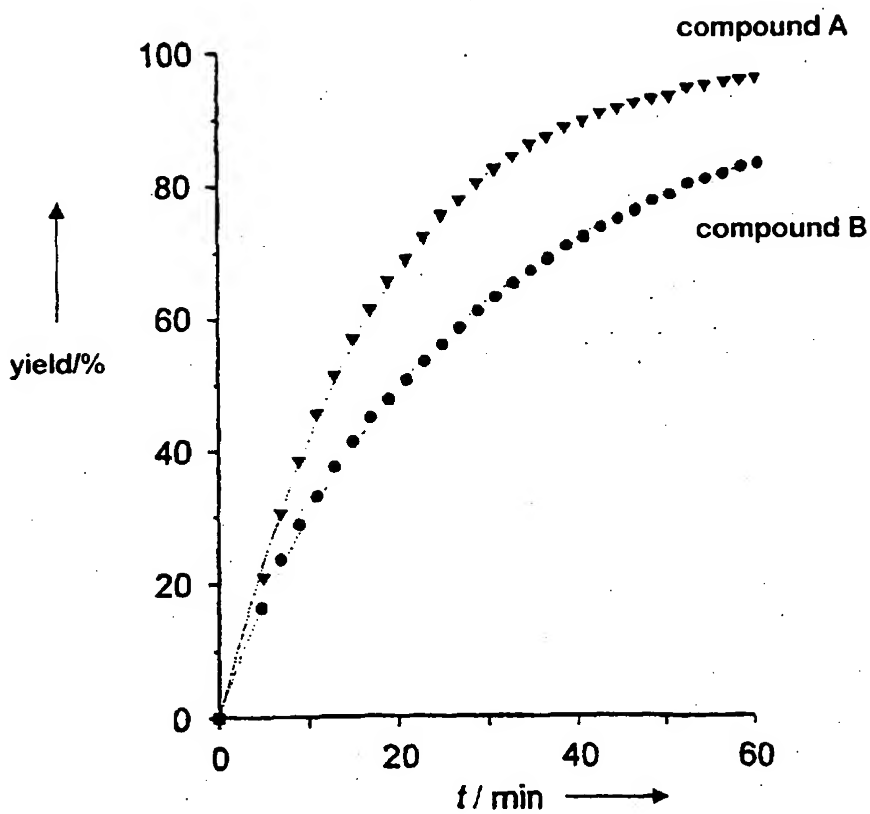
Typical reaction procedure for the metathesis of methyl oleate:

A solution of 3.6 mg (6.3 µmol) of 1 in 0.5 ml of dichloroethane was admixed with 1.06 ml (3.13 mmol) of methyl oleate, and the reaction mixture was placed in an oil bath at 60°C for 15 hours. GC/MS analysis

indicated the equilibrium of metathesis products shown in the reaction equation (7).

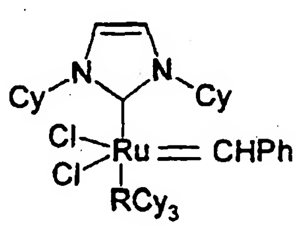
The metathesis of terminal and internal olefins was demonstrated by means of the homometathesis of 1-octene and methyl oleate. In the metathesis of methyl oleate as natural raw material, the thermodynamic equilibrium can virtually be reached within 15 hours using catalyst 1 at an olefin : catalyst ratio of 500 : 1. In the metathesis of 1-octene, 7-tetradecene was not obtained as sole reaction product in all cases. An isomerization of 1-octene to 2-octene detected by NMR spectroscopy and subsequent olefin metathesis is responsible for this fact. Homometathesis and cross-metathesis of 1-octene and 2-octene gave not only 7-tetradecene but also 6-tridecene as main by-product and small amounts of 6-dodecene, 1-heptene and 2-nonene. The product distribution is strongly dependent on the catalyst used. In the case of 2, 7-tetradecene was obtained virtually selectively; in contrast, the more active complex 1 gave 7-tetradecene in a selectivity of only 63% at a high conversion. The by-product obtained was essentially 6-tridecene from the cross-metathesis of 1-octene with 2-octene.

Ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene

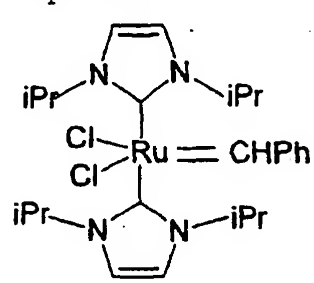


ROMP of 1,5-cyclooctadiene. NMR comparison of a ruthenium-dicarbene complex with a ruthenium-carbene-phosphine complex. (T = 25°C; 1.70 µmol of catalyst in 0.55 ml of CD_2Cl_2; [1,5-cyclooctadiene] / [catalyst] = 250:1).

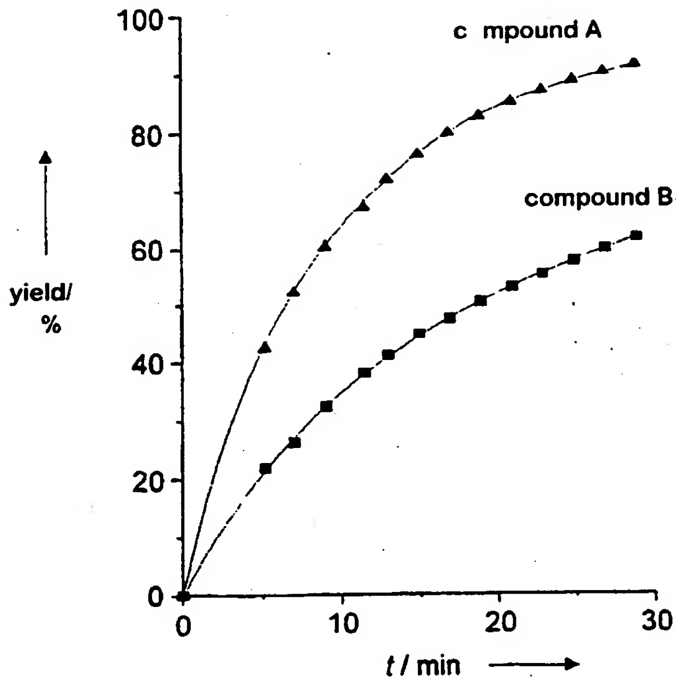
Compound A



Compound B

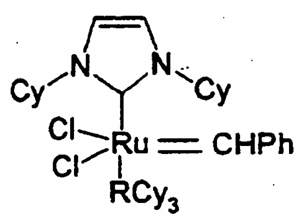


The same applies to ROMP of cyclooctene:



ROMP of cyclooctene. NMR kinetics of a ruthenium-dicarbene complex compared to a ruthenium-carbene-phosphine complex. (T = 25°C; 2.50 µmol of catalyst in 0.50 ml of CD_2Cl_2; [cyclooctene] / [catalyst] = 250:1.

Compound A



Compound B